

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Piotr KULA et al. Group Art Unit: 1793

Application No.: 10/531,477 Examiner: W. ZHU

Filed: April 15, 2005 Docket No.: 122041

METHOD FOR UNDER-PRESSURE CARBURIZING OF STEEL WORKPIECES

DECLARATION UNDER 37 C.F.R. §1.132

I, Dr. Piotr Kula, a citizen of Poland, hereby declare and state:

1. I have a degree in mechanical engineering, materials science and heat treating of metals which was conferred upon me by Politechnika Lodzka (Poland) in 1975.

2. I have been employed by Politechnika Lodzka since 1975 (since 1996 as professor), and I have had a total of 20 years experience in the field of steel carburizing.

3. I am a named inventor in the above-captioned patent application. I am familiar with the patent application.

4. I have a professional relationship with the Assignees, Seco/Warwick SP.ZO.O. and Politechnika Lodzka, of the above-identified patent application. In the course of that professional relationship, I received compensation for my work relating to research and

development regarding steel carburization. I am not being specially compensated for my work in preparing this Declaration.

5. I and/or those under my direct supervision and control have conducted the following experiments.

The following experimental results demonstrate that the presently claimed method for under-pressure carburizing steel achieves unexpected results by restraining the austenite grain

growth on the surface of the charge, while avoiding the formation of undesirable iron nitrides on the surface of the charge, when the active nitrogen carrier (e.g., ammonia) is (1) introduced into the vacuum furnace chamber during the preheating of the charge after the charge reaches at least 400°C (i.e., the lower limit) and (2) continuously introduced until the charge reaches the carburizing temperature, at which point the active nitrogen carrier is stopped and the carbon carrier introduction is begun (i.e., the upper limit).

THE LOWER LIMIT

Experiments 1-4 were conducted on three different low carbon steel grade charges at four different process conditions to confirm that the introduction of a nitrogen carrier only after a charge reaches a temperature of at least 400°C (i.e., the lower limit) unexpectedly inhibits austenite grain growth.

The first low carbon steel grade charge was comprised of C15. The second low carbon steel grade charge was comprised of 16MnCr5. The third low carbon steel grade charge was comprised of 18CrNiMo7-6. Each of the low carbon steel grade charges were treated in a 200 x 200 x 400 mm low-pressure vacuum furnace chamber at different process conditions. For the following experiments, 1000°C was selected as the carburizing temperature, and is thus referred to below as the upper limit for purposes of Experiments 1-4.

The four sets of process conditions were labeled as: Experiment 1, Experiment 2, Experiment 3 and Experiment 4. Experiment 1 consisted of conventional under-pressure carburizing without any introduction of ammonia gas during preheating of the charge to the carburizing temperature. Experiment 2 consisted of under-pressure carburizing with the nitrogen carrier in the temperature interval of 20 °C - 400 °C (i.e., starting below the lower limit). Experiment 3 consisted of under-pressure carburizing with the nitrogen carrier in the temperature interval of 400 °C - 1000 °C (i.e., representative of the claimed process). Experiment 4 consisted of under-pressure carburizing with the nitrogen carrier in the temperature interval of 20 °C -

1000°C (i.e., starting below the lower limit and continuing until the upper limit). The remaining parameters for Experiment 1, Experiment 2, Experiment 3 and Experiment 4 were kept constant and are summarized below in Table 1.

Table 1: Process Parameters for Experiment 1, Experiment 2,
Experiment 3 and Experiment 4

| Parameter | Experiment 1 | Experiment 2 | Experiment 3 | Experiment 4 |
|---|--------------------|--------------------|--------------------|--------------------|
| Ammonia Dosing Temperature Range | - | 20 °C - 400 °C | 400 °C - 1000 °C | 20 °C - 1000 °C |
| Ammonia flow | - | 50 l/h | 50 l/h | 50 l/h |
| Ammonia pressure | - | 26 mbar | 26 mbar | 26 mbar |
| Temperature of carburizing | 1000 °C | 1000 °C | 1000 °C | 1000 °C |
| Time of boost | 20 min | 20 min | 20 min | 20 min |
| Time of diffusion | 5 min | 5 min | 5 min | 5 min |
| Acetylene flow | 72.9 l/h | 72.9 l/h | 72.9 l/h | 72.9 l/h |
| Ethylene flow | 72.9 l/h | 72.9 l/h | 72.9 l/h | 72.9 l/h |
| Hydrogen flow | 124.2 l/h | 124.2 l/h | 124.2 l/h | 124.2 l/h |
| Pressure | 3 - 8 mbar |
| Charge area | 0.4 m ² | 0.4 m ² | 0.4 m ² | 0.4 m ² |

After treatment under the process conditions of Experiments 1-4, the austenite grain size, the austenite mean grain diameter and case depth was measured for each of the three steel grades (i.e., C15, 16MnCr5 and 18CrNiMo7-6). The results are summarized below in Tables 2-4, respectively.

Table 2: Austenite Grain Size* of Under-Pressurized Steel Charges According to ASTM E1382-97

| Grain Size ASTM E1382-97 | C15 | 16MnCr5 | 18CrNiMo7-6 |
|-----------------------------|-----|---------|-------------|
| Experiment 1 | 5.8 | 7.5 | 8.5 |
| Experiment 2 | 5.7 | 7.5 | 8.4 |
| Experiment 3 | 6.6 | 10.2 | 9.0 |
| Experiment 4 | 6.5 | 9.5 | 8.7 |

* Austenite grain size here refers to grain size (G) in the formula: $m=8 \times 2^G$, where m is number of austenite grains per square millimeter.

Table 3: Mean Austenite Grain Diameter of Under-Pressurized Steel Charges According to ASTM E1382-97

| Mean Grain Diameter ASTM E1382-97 | C15 | 16MnCr5 | 18CrNiMo7-6 |
|--------------------------------------|--------------------|--------------------|--------------------|
| Experiment 1 | 47.3 μm | 26.2 μm | 18.5 μm |
| Experiment 2 | 49.0 μm | 26.2 μm | 19.2 μm |
| Experiment 3 | 35.8 μm | 10.3 μm | 15.6 μm |
| Experiment 4 | 37.1 μm | 13.1 μm | 17.3 μm |

Table 4: Case Depth of Under-Pressurized Steel Charges

| Case Depth | C15 | 16MnCr5 | 18CrNiMo7-6 |
|---------------------|---------|---------|-------------|
| Experiment 1 | 0.54 mm | 0.72 mm | 0.62 mm |
| Experiment 2 | 0.57 mm | 0.52 mm | 0.68 mm |
| Experiment 3 | 0.70 mm | 0.76 mm | 0.83 mm |
| Experiment 4 | 0.62 mm | 0.75 mm | 0.76 mm |

The microstructures for each of the three treated steel grades treated under the process parameters for Experiment 1, Experiment 2, Experiment 3 and Experiment 4 were etched with Mi7Fe and are illustrated below in Figures 1-3, respectively.

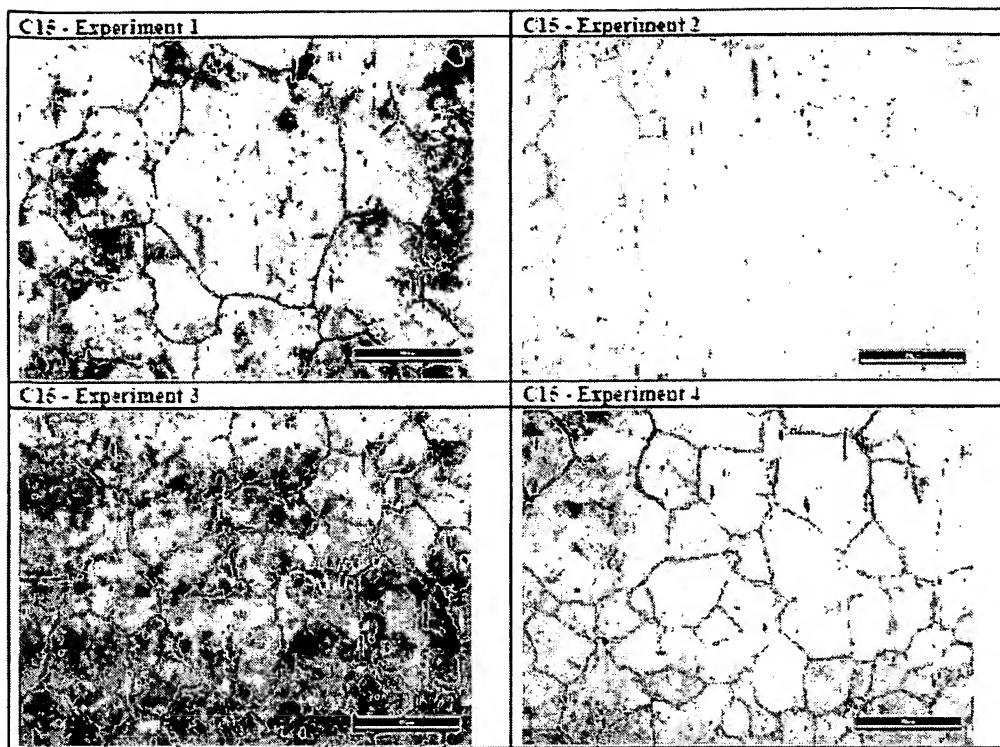


Figure 1: Microstructure for C15 Steel Treated Under Experiments 1-4

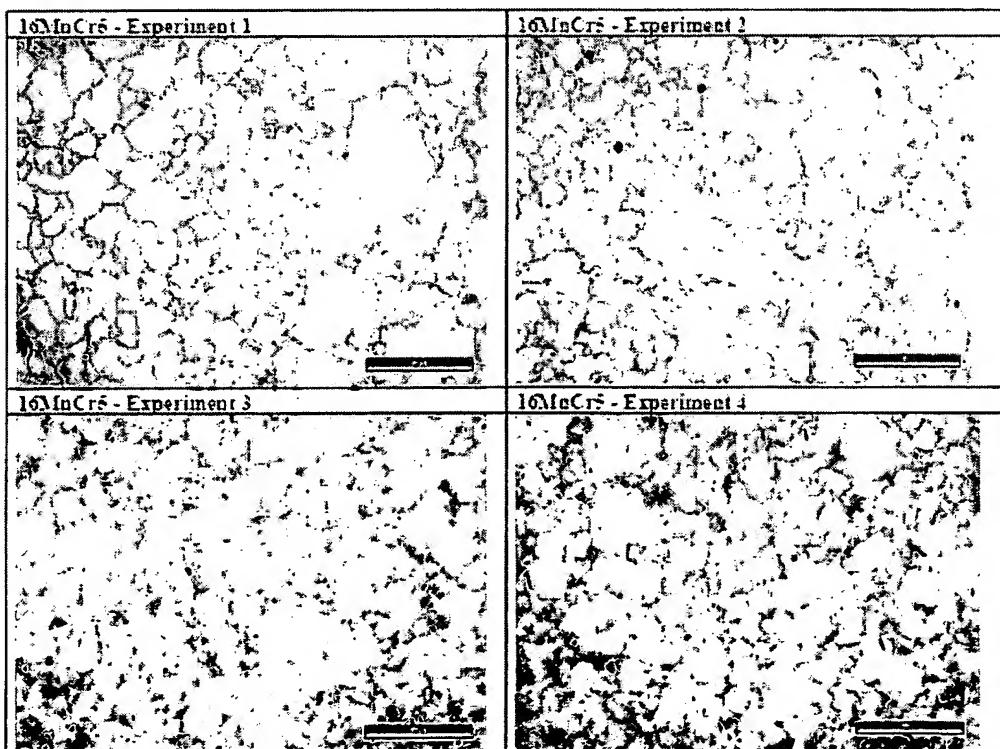


Figure 2: Microstructure for 16MnCr5 Steel Treated Under Experiments 1-4

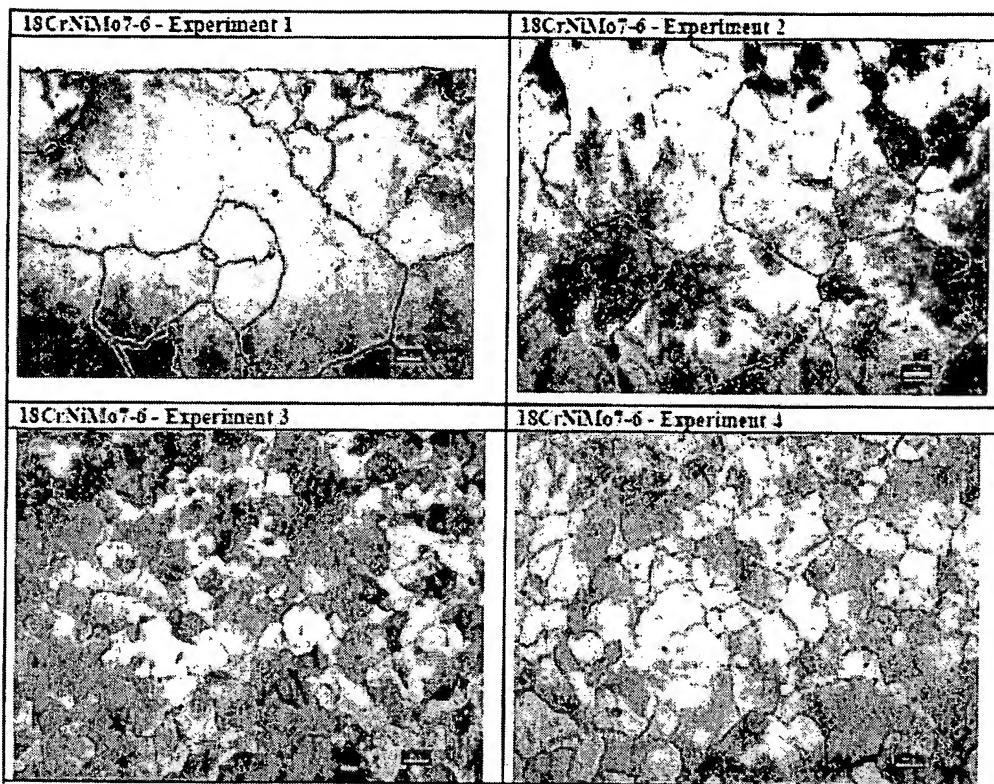


Figure 3: Microstructure for 18CrNiMo7-6 Steel Treated Under Experiments 1-4

As shown above in Tables 2 and 3 and visually confirmed by Figures 1-3, the steel charges that were subjected to Experiment 3 (i.e., the claimed method) possessed both (1) the largest austenite grain size and (2) the finest austenite mean grain diameter, due to the reciprocal relationship between austenite grain size and austenite mean grain diameter.

Furthermore, as shown above in Table 4, the steel charges of Experiment 3 achieved the deepest case depth. A steel charge with a deep case depth will accelerate the carburizing process and allow the carburizing gas to more deeply penetrate the surface of a charge.

As such, the experimental results demonstrate that the presently claimed method for under-pressure carburizing a steel charge mixture by introducing an active nitrogen carrier into the vacuum furnace chamber during the preheating of the charge after the charge reaches at least 400 °C unexpectedly restrained the austenite grain growth on the surface of steel charge.

THE UPPER LIMIT

Experiments 5-8 were conducted to confirm that continuously introducing the nitrogen carrier (i.e., ammonia) from at least 400°C until the steel charge reaches the carburizing temperature, at which point the nitrogen carrier is stopped and the carbon carrier introduction is begun, unexpectedly restrains the growth of austenite grains on the steel charge, while avoiding the formation of undesirable iron nitrides on the surface of the charge.

Experiment 5 consisted of "prenitriding", i.e., introducing ammonia gas beginning at 400°C into a low-pressure vacuum furnace chamber containing a 16MnCr5 charge. The ammonia gas was continuously introduced into the vacuum furnace chamber until the temperature of the steel charge reached the carburizing temperature of 1000°C. At this point, the flow of ammonia gas was stopped and the introduction of the carbon carrier began.

Experiment 6 consisted of the same "prenitriding" treatment to a 16MnCr5 charge except that carbon carrier was not introduced into the vacuum furnace chamber. The process parameters for Experiment 5 and Experiment 6 are summarized below in Table 5.

Table 5: Process Parameters for Nitrogen Distribution Measurements
of Experiment 5 and Experiment 6

| | Total Carburizing Time | | Prenitriding Interval (°C) | Carburizing Temperature (°C) | Ammonia Pressure (mbar) | Boost Pressure (mbar) | Steel Grade |
|--------------|------------------------|-----------|----------------------------|------------------------------|-------------------------|-----------------------|-------------|
| | Boost | Diffusion | | | | | |
| Experiment 5 | 9 min. | 20 min. | 400-1000 | 1000 | 26 | 3-8 | 16MnCr5 |
| Experiment 6 | - | - | 400-1000 | - | 26 | - | 16MnCr5 |

The nitrogen concentration at various distances from the charge's surface was measured for Experiment 5 and Experiment 6 and is illustrated below in Figure 4.

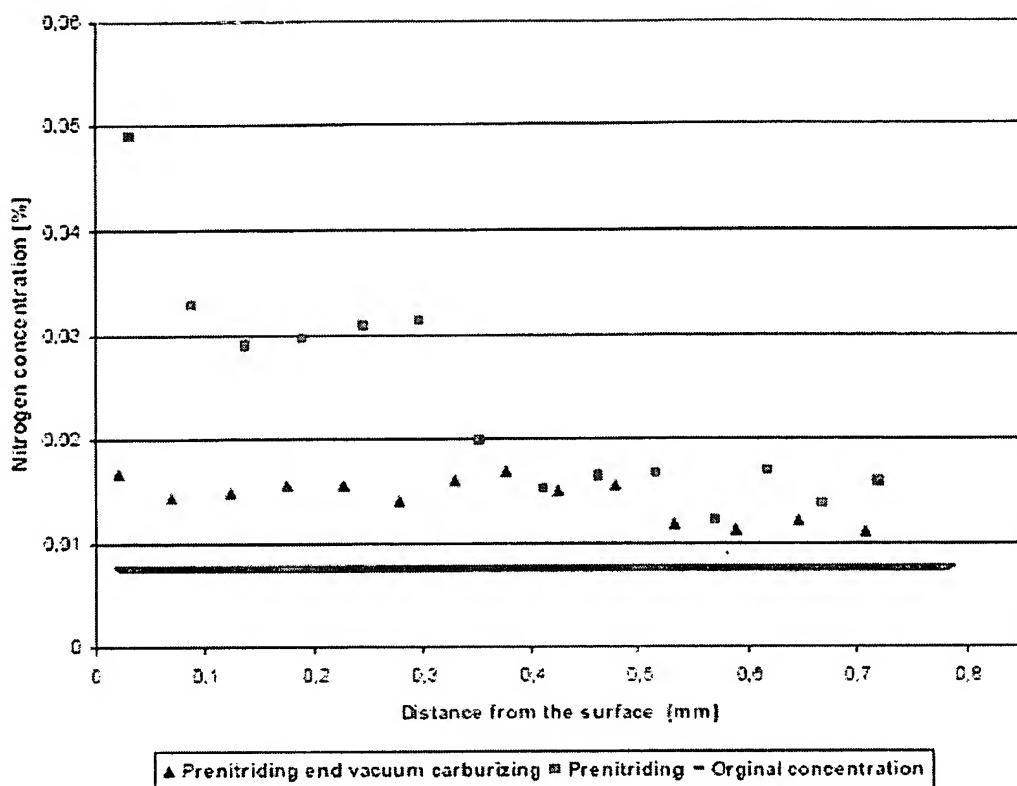


Figure 4: The Nitrogen Concentration on the Surface of a 16MnCr5 Charge After (1) Under Pressure Carburizing Preceded by Prenitriding (i.e., Experiment 5 - triangles) and (2) Prenitriding Only (i.e., Experiment 6 - squares).

As shown above, prenitriding followed by the introduction of the carbon carrier permits nitrogen to be homogeneously distributed in the charge. This increases the nitrogen concentration over the original charge and thus inhibits austenite grain growth while maintaining a nitrogen concentration at the surface of the charge that is low enough to prevent the formation of disadvantageous iron nitrides.

Experiment 7 was performed on a charge comprised of 15CrNi6, in which the charge was subjected to a treatment including introducing a nitrogen carrier at a temperature of 400°C. The nitrogen carrier was continuously introduced until the charge reached the carburizing temperature (980°C in this case), at which point the nitrogen carrier was stopped and the carbon carrier introduction started. The charge was then quenched and etched with NiFe (Nital).

Experiment 8 was performed on a same type of charge and subjected to a treatment including introducing a nitrogen carrier at a temperature of 400°C. The nitrogen carrier was continuously introduced throughout the process. When the charge reached the carburizing temperature (980°C in this case), the nitrogen carrier was not stopped, and the carbon carrier introduction was started. As with Experiment 7, the charge was then quenched and etched with MilFe (Nital).

Figure 5(a) below represents a light microscopy picture of the microstructure of the charge following treatment in Experiment 7 and Figure 5(b) represents a light microscopy picture of the microstructure of the charge following treatment in Experiment 8.

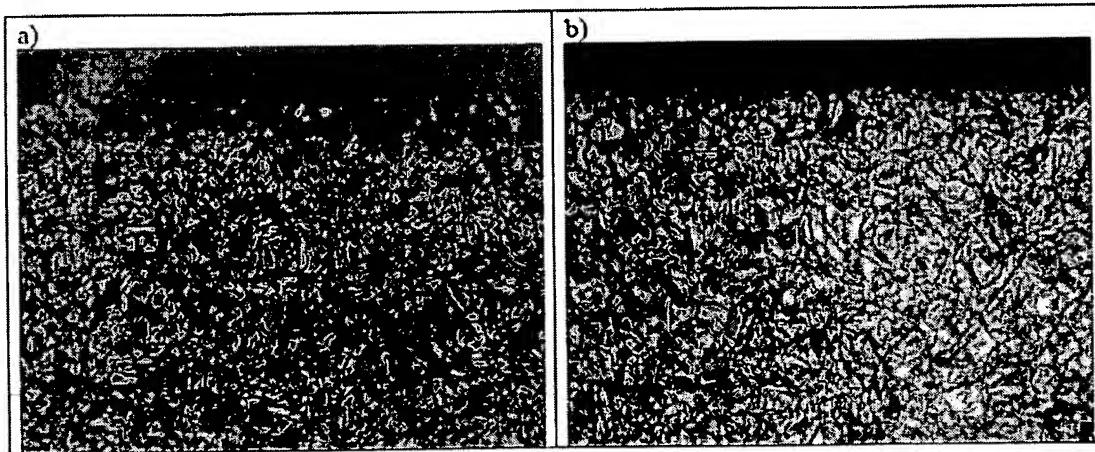


Figure 5: Microstructure After Prenitriding of Under-Pressure Carburized (a) and Under Pressure Carbonitrided (b) 15CrNi6 Steel at 980°C (Magnification x500).

In Figure 5(b), the large amount of white fields, representing retained austenite on the surface of the charge, are caused by the high concentration of nitrogen (about 0.16%) at the charge's surface. This large amount of retained austenite decreases the hardness of the charge and thus results in a steel charge that is too soft. However, the charge of Figure 5(a) has a lower surface concentration of nitrogen (about 0.02%) with fewer white fields representing retained austenite on the charge surface. As such, continuing the flow of a nitrogen carrier after the charge reaches a carburizing temperature (i.e., simultaneously with a carbon carrier) increases the

nitrogen content and causes the disadvantageous stabilization of the retained austenite of the surface, particularly when compared to a charge treated in accordance with the claimed process (i.e., Figure 5(a)).

As such, the experimental results demonstrate that the presently claimed method for under-pressure carburizing a steel charge mixture by continuously introducing the nitrogen carrier from at least 400°C to until the charge reaches the carburizing temperature unexpectedly restrained the austenite grain growth on the surface of steel charge while avoiding the formation of undesirable iron nitrides that adversely affect the microstructure of the charge.

6. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date:

24. 06. 2008

P. Kula

Dr. Piotr KULA